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(54) Title: MULTI LAYER POLYOLEFINIC TUBE

(57) Abstract: Multi layer tube of polyolefin characterized by at least two layers, concentric to tube centre line, of different material, where inner layer (i) of the tube is of polyolefin selected group consisting of low density polyethylene (a) of density 0,910 up to 0,930 g/cm^3, linear low density polyethylene (b) of 0,915 up to 0,940 g/cm^3, high density polyethylene (c) of 0,940 up to 0,975 g/cm^3 density and isotactic polypropylene (d). The second layer (ii) outwards the centre line of tube is a mixture of polyolefins containing 50 % of mass polyolefin elements which creates inner layer of tube and at most 50 % low density polyethylene (a) of 0,910 up to 0,930 g/cm^3 density and/or linear low density polyethylene (b) of 0,915 up to 0,940 g/cm^3 and/or high density polyethylene (c) of 0,940 up to 0,975 g/cm^3 density and/or izotactic polypropylene (d).

MULTI LAYER POLYOLEFINIC TUBE

Technical Field

The invention concerns of multi layer tubes of polyolefine

Background Art

Plastics became the most favorit material for manufacture of piping systems for gas and fluids conducting currently. Plastics satisfies application demands of this group material properties generally. Main material demands for manufacture of tube systems piping components are following: high chemical resistence, high mechanical strength and technologicaly easy workability.

Demands above result from following main needs: as long as possible life of piping systems at the lowest cost (price). The high chemical resistence giving long term corrosson resistence. The high mechanical strength is the main premise against long term mechanical stress (inner event. outer over-pressure). The good workability is then the main condition for of stabile quality when individuel piping components are manufactured, which includes various tube and tube fitings in very wide diameter range generally.

Most current material for water conduit pipes, draining systems and gas piping is high density polyethylen (HDPE) and non softened polyvinylchlorid (PVC),which are followed as far as extent is concerned by polypropylene (PP), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), medium density polyethylene (MDPE) a net polyethylene (PEX) and polybuthylene (PB). Tubes of thermo plastics are manufactured by extrusion of melted material.

The highest demands on long life mechanical strength and hygienic unobjectionability are layd down on material of outer and inner water conduits pressure tubes. Any plastics is charakterized by certain material properties, which limit its applicability for processing of piping elements. The

most common material of outer piping elements are HDPE, LDPE, and PP. Specific demands on inner hot water conduit pipes elements (fittings) are required.

Materials used for fabrication of inner water conduits fittings differ in accordance if they are used to conduct cold (drink) or hot water. The simpler case is cold water piping , for which tubes and fittings of HDPE are used (similar for outer cold water piping), but more frequently PP is used

Permanent temperature of 60° C at 0,9 Mpa is supposed in distribution piping systems of hot service water in buildings. There is not possible to use the same tubes and fittings here as for cold water distribution.The long term practical experience approved, that long term temperature and pressure stress brings a brittle breakage when improper tube material is used.

Common used material for fabrication of tubes and fittings for distribution hot water pipings proved to be PP Type 3 (in accordance with DIN 8078). This type of PP is a copolymer of propylene with some alfa olefines , e.g. 1-hexen or 1- octen. This type PP has much lower tendency to be liable to brittle breakage destruction in comparisson with the other PP types thanks its modifyed cristaline phase. The main unadvantage uf this type of PP is the higher price in comparison with the others PP types.

The biggest unadvantage currently used plastics materials up to now is their tendency to be liable to destruction at long term overpresure loading.

The effort to eliminate this unadvantage led to development of three layer tubes with two shift- inner and outer surface plastic coating **of** metalc core (aluminium is mostly used). The metalic core of tube is manufactured by coiling of sheet core which increases essentially tube overpreassure resistance with no regard to water temperature. Coating of metalic core by pastic surfaces ensures then health unobjectionability and chemical resistence required.

PB or net forming PE (PEX) is used for coating. Essential advantage of this tube is an easy instalation of the piping system (no fittings are almost required), the piping is formed downright on the site by simillar processing method as used when leaden tubes were installed with the same temperature and mechanical resistence.

The principle unadvantage of the tube above is considerably higher price and tendency to separate metalic core from plastics shifts when the piping is remitted to long term temperature and pressure changes of distributed media. (water).

Multi layer tube of polyolefine in accordance with this invention eliminates these unadvantages currently used tubes of plastics, which have relatively low resistance against inner overpressure and considerably higher price when manufactured to provide better properties it means higher resistence to constant inner overpressure.

Disclosure of invention

The subject of the invention is multi layer tube of polyolefime consisting from two layers of different material concentric to centre line of the tube, where inner layer of the tube (i) is created by polyolefine assorted from a group containing material of low density polyethylene (a) of 0,910 to 0,930 g/cm^3 density, linear low density polyethylene (b) of 0,915 to 0,940 g/cm^3 density, high density polyethylene (c) of 0,940 to 0,975 g/cm^3 density, and of isotactic polypropylen (d). The second (outside) layer (ii) - outwards centre line of the tube is a mixture of polyolefines containing 50 % of mass polyolefines at least, which creats inner layer of the tube and 50 % at most of low density polyethylene (a) of density 0,910 up to 0,930 g/cm^3 and/or linear low density polyethylene (b) of 0,915 up to 0,940 g/cm3 density and/or high

density polyethylene (c) of 0,940 to 0,975 g/cm^3 density and/or isotactic polyprophylene (d)

The tube of polyolefines in accordance with this invention described could also be made with three layers adventiously, when third layer outwards centre line contains 50% of polyolefines of (a) type at least and/or (b), and/or (c) and/or (d) , which is contained in polyolefine mixture in second layer (ii).

The second layer (ii) of the tube in accordance with the invention can contain from 2 % up to 25% of mass compatible additives , which is created by ethylene-polypropylene copolymer of medium molar mass M_w = 20000 g(mol up to M_w = 80000 g/mol, having 12 % at least and 80 % at most of molar prophylene.

Outer layer of rhe tube can contain 0.5 % up to 15 % anorganic pigment in accordance with the invention, which could consist of carbon or soot respectively, titan oxide, zinc oxide and/or it can contain also 0.1% to 1.5 % anorganic oxidant mass on the base of fenol substituted and/or 0,3 to 2.5% organic fosfid mass.

Multi layer tube principle design to the invention constitutes several polyolefine materials having a good inter phase adhesion and eliminates present most considerable unadventage plastics tubes represented by easy brittle breakage widening through tube wall cross section. The brittle breakage widening is possible to eliminate by appropriate combination of polyolefine materials fastening up concentricaly oriented other layers of inner wall, without essential price increasing. There is possible to improve mechanical properties of the tube in accordance with the invention using polyolefine compatilizators additives in second layer, especially of ethylene-propylene copolymers.

Another one advantage of multi layer polyolefine tubes to this invention is easy reachable weather resistance with tubes having the outer layer of

temperature stabilized material, without any negative influence on hygienic properties of water, which could arise from reaction components and products of stabilizing penetrated into system of water conducting.

Weather resistance of the tube invented is guaranted by anorganic pigments addition to eliminate efect of sun radiation. Titan oxide, zinc oxide and carbon in form of soot and/or antioxidants is used for this purpose. Creation of polyolefine precursors degradation is also possible to avoid by fenols substituted or synergic combination substituted fenols with organic fosfids.

Another one of multi layer tube of polyolefine advantage in accordance with this invention is recycling of polyolefine remainders and scrap utilized for a new tubes production, without lost or decreasing of material properties.

Recyclants utilizing is advantageous especially for tube outer layer manufacture under the supposition the inner wall of the tube is made of virgin polyolefine and penetration or difusion eventual deleterious substances from recyclate into conducted water is avoided. Mechanical properties improvement of recyclate of outer layer is possible by additives of polyolefine compatibilizators - ethylene copolymers especially.

Polyolefine recyclantes exploitation as material for tube manufacture to this invention is advategeous from ecological point of view, also of valuation and energetical content utilization of this raw material.

The optimal technology for manufacture of multi layer tubes in accordance with this invention is co extrusion.

Manufacture of multi layer tubes and some advantages of this product is illustrated in following examples:

Examples

EXAMPLE no. 1:

The two layer tube has been manufactured by co- extrusion of outside diameter 63 mms. Tube total wall thickness of 3 mms consisted of 1 mm **inner layer** of virgin low density polyethylene of 0,921 g/cm^3 mass (commercial name Bralen FB 2-17) and **outer layer** of polyethylene recyclant mixture containing low and high density polyethylen in mass proportion of 2: 3.

Material of outer layer has been added by 2.0% titan oxide of rutile type, 1,2 % soot, 0,2% fenolic antioxidant (commercial name Irganos 1010) and 0,6 % of organic fosfide (commercial name Irgafos 168). The tube manufactured has been tested on resistence against constant inner overpressure. Table no. 1 compares test results of constant inner overpressure resistance at 20°C and starting stress of 6,9 MPa of two layer tube described above, manufactured in accordance with invention with the tube manufactured of low density polyethylene Bralen FB 2-17. The comparison made in table shows that the time until rupture of two layer tube to the invention is practicaly the same as of the tube made from virgin low density polyethylene, in spite of it that this two layer tube was made of less valuable material (recyclante).

TABLE no. 1

Tube (material)	Time until rupture (min.)
Low density polyethylen (Bralen FB 2-17)	66 min.
In accordance with invention (example no.1)	70 min.

EXAMPLE no. 2

The two layer tube has been manufactured by co- extrusion of outside diameter 63 mms. Tube total wall thickness of 3 mms consisted of 1,2 mm inner layer of virgin low density polyethylene of 0,919 g/cm^3 mass (commercial name Bralen RA 2-19) and outer layer of waste polyolefine recyclante mixture containing low and high density polyethylen and izotactic polypropylen in mass proportion of 3 : 2 : 2. Outer layer material has been added 5% ethylene propylene copolymer of medium molar mass M_w = 360000 g/mol containing 33 % of molar propylene (commercial name Dutral Co 038) and 0,6 % organic fosfid (commerctial name Irfagos 168). The tube manufactured has been tested on resistence against constant inner overpressure. Table no. 2 compares test results of constant inner overpressure resistance at 20 ° C and starting stress of 6,9 MPa of two layer tube described above, manufactured in accordance with invention and compared tube manufactured of low density polyethylene Bralen RA-2-19 and tube manufactured of recyclate only of mixture containing high density polyethylene, low density polyethylene and izotactic polypropylene in mass proportion 3 : 2 : 2 and 5 % compatibilizator (ethylene –propylene copolymer) which was also used for manufacture of the tube in accordance with the invention.

The comparison made in table shows that the time until rupture of two layer tube to the invention is longer then of the tube made of virgin low density polyethylene.

TABLE no. 2

Resistance against constant inner overpressure of 63 mms outside diameter

and 3,0 mm wall thickness tube at 20 ° C and starting pressure of 6,9 MPa

Tube (material)	Time until rupture (min.)
Low density polyethylen (Bralen RA 2-19)	68 min.
In accordance with invention (example no.2)	75 min.

EXAMPLE no. 3

The three layer tube has been manufactured by co- extrusion of outside diameter 75 mms. Tube total wall thickness of 4,3 mms consisted of 1,0 mm inner layer of virgin izotactic polypropylen (commercial name Mosten 55 292) ,

second layer of 2,3 mm thickness of mixture 65 % izotactic polypropylene , 25 % high density polyethylene and 10 % ethylene propylene statistic copolymer of medium molar mass of M_w =390000 g/mol, containing 38,5 % molar propylene and the third (outer) layer of 1,0 mm thickness of virgin high density polyethylene (commercial name Liten PL 10). The tube manufactured has been tested on constant overpressure resistence . Comparison of tests is made in Table 3. Resulted resistence against constant overpressure has been obtained at 20 ° C, under starting stress of 21,0 Mpa and at 80 °C under 8,4 MPa of above desribed three layer tube to this invention and the tube of the same dimensions of izotactic polypropylene (commercial name Mosten 55 292)

The test results in Table no. 3 show , that time lasting to rupture of three layer tube is longer then the time to rupture of tube of virgin high density polyethylene.

TABLE no. 3

Comparison of resistence against constant inner overpressure of tubes of 75 mm diameter with 4, 3 mm wall thickness at 20 ° C and starting stress of 21 MP a and at 80 ° C and starting stress of 8,4 M P a.

Tube (material)	Time to rupture (min.)	
	at 20° C and starting stress of 21,0 M P a	at 80° C and starting stress of 8,4 Mpa
of polypropylen (Mosten 55 292)	65	62
in acc. with invention	78	73

Industrial availability

Multilayer tubes of polyolefine to this invention are available as components for inside and outside water conduit piping and draining systems in civil engineering also as protection components of cabel distribution systems , in chemical and food industry as well as piping systems of fluid and gas conveying in many industrial branches.

Claims

1. Multi layer tube of polyolefine designated by:
at least two layers , concentric to tube centre line, of diferent material , where inner layer (i) of the tube is of polyolefine selected of group consisting of low density polyethylene (a) of density 0,910 up to 0,930 g/cm^3 , linear low density polyethylene (b) of 0,915 up to 0,940 g/cm^3, high density polyethylene (c) of 0,940 up to 0,975 g/cm^3 density and isotactic polypropylene (d) and the second layer (ii) outwards of the centre line of tube is mixture of polyolefines containing 50 % of mass polyolefine elements , which creates inner layer of tube and at most 50 % low density polyethylene (a) of 0,910 up to 0,930 g/cm^3 density and/or linear low density polyethylene (b) of 0,915 up to 0,940 g/cm^3 and/or high density polyethylene (c) of 0,940 up to 0,975 g/cm^3 density and/or izotactic polypropylene (d)

2. Multi layer tube of polyolefines in accordance with demand 1 above designated by that it contains the third (iii) layer outwards of centre line of tube, of material containing at least 50 % polyolefine type (a) and/or (b) and/or (c) and /or (d) which is contained in polyolefine mixture in second layer (ii)

3. Multi layer tube of polyolefines in accordance with demands 1 and 2 above designated by that the second layer (ii) contains 2 up 25% mass elements ethylene-peopylene copolymer of medium molar mass M_w=20000 g/mol up to M_w= 80000 g/mol having 12 % but 80 % at most of molar propylene.

4. Multi layer tube of polyolefines in accordance with demands 1, 2 and 3 above, designated by that the last outer layer of tube outwarts tube centre line contains 0,5 up to 12 % anorganic pigment mass elements and/or 0,1 to 1,5 % organic antioxidant mass elements on the base of subtituted fenol
and/or 0,3 to 2,5 % organic fosfid elements.

INTERNATIONAL SEARCH REPORT

International Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B32B27/32 B32B1/08 F16L11/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B32B F16L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 344 714 A (SU TIEN-KUEI) 6 September 1994 (1994-09-06) claims 1,3,4 column 2, line 6 -column 3, line 2 column 3, line 18 - line 55 ---	1-4
A	DE 42 16 516 A (HAAGA KARL) 25 November 1993 (1993-11-25) claims 1-6 column 1, line 51 - line 65 column 2, line 21 - line 62 column 3, line 60 -column 4, line 34 --- -/--	1-4

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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